R&D 5910B-EE-01

(1)

ARON VECHT & ASSOCIATES

THE PREPARATION OF ACEL THIN FILMS

Principal Investigator: Professor Aron Vecht

R&D 5910B-EE-01 Contract DAJA45-89-0005

FINAL REPORT

MAY 1990

The research reported in this document has been made possible through the support and sponsorship of the US Government through its European Research Office of the US Army. This report is intended only for the internal management use of the Contractor and the US Government.

Aron Vecht
Surjit S Chadha
David W Smith

Background

This is the final report under the USAEC Contract Number DAJA45-89-C-0005. Under this contract, six interim reports have been submitted (1-6). The main objectives of the contract can be summarised as follows:

a) To deposit high quality ZnS thin films by MOCVD
b) To dope the ZnS thin film with Mn
c) To deposit high quality dielectric films using a novel spray pyrolysis process
d) To evaluate optimised insulator/ZnS.Mn/insulator structures
e) The fabrication of large area XY matrix ACEL structures.

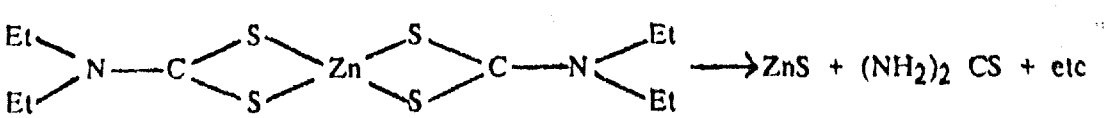
Introduction

Although thin film ACEL devices have become commercially available, the number of companies producing these displays has continued to diminish. The cause of their demise was not display performance, as both sufficient brightness and efficiency has been achieved, but the low return on the heavy capital investment due to the poor yields obtained in production. In order to make ACEL thin film devices more viable, the capital investment needs to be low and/or the production yields high. We believe that opting for relatively expensive sputtering or ALE techniques as the sole methods of fabricating EL structures, is both commercially and scientifically ill-advised. We have therefore spent considerable effort in developing cheaper alternative techniques for thin film deposition. In the area of ACEL thin films, a large part of our recent investigations has been funded by USAEC. The results of a two year exercise are outlined on the following pages.

Results

1) Optimisation of ZnS Thin Films

Unlike the conventional MOCVD processes for the growth of zinc sulphide thin films described in the literature, i.e. diethyl zinc + H_2S, we opted for the Zn diethyl dithiocarbamate 'fission' reaction for the deposition of thin films of ZnS. This compound decomposes at low temperatures around 400°C as follows:



The compound is stable, easily prepared and purified, and has a low level of toxicity when compared to alkyl metal precursors. A large range of metal diethyl dithiocarbamate complexes can be prepared. Initially, it was thought that they could also be used as dopant precursors. Unfortunately, manganese dithiocarbamates did not prove entirely satisfactory and other complexes have been chosen which yield better results.

The low pressure MOCVD system used is shown diagrammatically in Fig. 1. ZnS thin films were characterised by SEM-EDAX and XRD. A typical XRD trace of the ZnS is shown in Fig. 2 indicating that the crystallite size is ~70nm.

When we had optimized the deposition conditions, the appearance of the low pressure (LP) MOCVD ZnS films was found to be good, showing the required transparency and uniformity. As a result of an extensive number of experiments, we arrived at the following conditions for optimum film quality:

Source temperature	160°C
Substrate temperature	400-410°C
Deposition time	6-7 hours
Pressure	3 torr

2) Mn doping of ZnS Thin Films

a) Mn organometallic precursors

The literature on Mn doping of MOCVD deposited thin films of ZnS pointed to the use of methyl cyclopentadienyl (Mn) tricarbonyl (TCM). The initial choice of this compound as our preferred Mn dopant was, however, unfortunate as the results were less than satisfactory. Considerable time and effort was spent at optimising conditions, but no real improvement was obtained. It became clear that the films produced using TCM contained considerable concentrations of impurities. This is probably due to the reaction temperatures used in this system being investigated. It should be recalled that the deposition temperature used in our system is over 100°C lower than that reported elsewhere. After careful re-evaluation, we initiated an exercise aimed at the use of other possible Mn precursors. A wide variety of Mn compounds was tried. These included Bis-(cyclopentadienyl)-Mn (MnCPD), $Mn(Et_2dtc)_3$, $Mn_5(CO)_{10}$, Di pyridine manganese (II) chloride and $Mn(CO)_3\ C_5H_5$.

perform 50

b) Metal interlayers

It was found that if a thin film of Mn metal was evaporated on top of the Al_2O_3 dielectric layer before ZnS deposition, the Mn reacted with the Zn ddc vapour resulting in the diffusion of the Mn into the ZnS lattice.

The results of the Mn doping by TCM, Mn metal and MnCPD are shown in Fig. 3. It is clear that considerable work is still required to obtain optimum efficiency and light output.

c) Mn vapour reaction

One of the other interesting features of the ZnS.Mn films prepared with Mn metal layers, was the extensive lateral Mn vapour phase diffusion which was observed. Some recent samples (e.g. AVA 372) were therefore prepared using a metal coated slide sitting in the path of the reactive vapour. The results indicate that the Mn is transported to the substrate and activation takes place. Results are quite promising and may obviate the need for specially prepared organometallic organic precursors. (Fig. 4).

d) TCM decomposition

We observed that if some oxygen was bled into the deposition chamber when TCM was used as the dopant, considerable improvement in the EL characteristics were obtained. It may well be that the oxygen breaks up the TCM complex to yield reactive Mn.

In summary, it should be noted that only a very limited number of variables were tried in all the above experiments and the results obtained should serve as indicators for more systematic investigations to be carried out in the future.

3) The fabrication of Dielectric Films

The aerosol spray pyrolysis method developed by Aron Vecht & Associates, previously described (7), is illustrated in Fig. 5 and was used throughout for the preparation of the dielectric layers. Insulating films of Y_2O_3 (using $Y(acac)_3$ solution at 0.05M in methoxy ethanol), Al_2O_3 (Al(acac)), MgO and Al_2O_3-Y_2O_3 composites were prepared, using a novel spray pyrolysis system. Most were grown in a substrate temperature range of 400-450°C. The beauty of this system is that films of good quality can be deposited at high growth rates.

It was found that Al_2O_3 insulating layers were adequate for most purposes for preliminary measurements. These were used in standard experiments for evaluating the variables in the ZnS.Mn deposition.

4) Combined Insulator/ZnS.Mn/Insulator Stacks

Most of the early films were characterised at 1000Hz. However, recently the USAEC indicated the importance of luminance measurements at 100Hz. We found that Al_2O_3/ZnS.Mn/Al_2O_3 stacks were unstable at this excitation frequency. Evaluation of other insulating materials revealed that MgF_2 as the top dielectric was admirably suited for low frequency operation. These layers were deposited by thermal evaporation. At 100Hz excitation, luminance in excess of 100 ftL was observed, see Fig. 6. MgO layers were found to give unstable devices but exhibited very low avalanche voltages.

The stability of Al_2O_3/ZnS.Mn/Al_2O_3 stacks has been assessed at USAEC and is shown in Fig. 7. Over 50 ftL was measured at 100Hz using 250V pulses of 30μs duration as shown in Fig. 8.

5) Large Area Devices

This is one area in which progress has not been made, mainly due to the time spent in solving the problem of efficient Mn doping and insufficient funds. The normal substrate dimensions are 2.5cm x 2.5cm but normally 9 substrates are coated simultaneously in the LPMOCVD apparatus. Hence, the 7.5cm x 7.5cm size substrates could be readily accommodated but experiments have not yet been tried on this scale. The spray pyrolysis system has not been used for simultaneous large area coating and will require fundamental redesigning.

Conclusions and Pointers to Future Work

Following a rather slow start, we have met most of our major objectives outlined at the beginning. The progress most probably would have been even greater had we not been stuck with using TCM as the Mn dopant. Despite that, we managed to increase luminance from around 10 ftL to nearly 500 ftL in just six months, as well as achieving 100 ftL at 100Hz. Along the route to new Mn source materials, we have discovered that under the reactive phase deposition conditions present in our system, Mn metal films can also be used quite effectively as the Mn dopant source. The process needs optimisation, but already over 200 ftL have been achieved, which is significantly better than TCM.

This may have possible implications for other colour ZnS thin films, e.g. by using thin films of rare earth. The technique may well be extended to the preparation of doped CaS, BaS or MgS thin films.

The work on insulators has been promising and leads to fairly stable films, but requires further effort for low frequency excitation. It is possible that multiple insulator stacks may be required.

It should be noted that in this work, no effort was devoted to increasing device contrast and this should form an integral part of any future programme.

Large area XY matrix structures have not been studied, though 7.5cm x 7.5cm ZnS films can readily be deposited.

References

1) The Preparation of ACEL Thin Films, First Interim Report, December 1988
2) The Preparation of ACEL Thin Films, Second Interim Report, March 1989
3) The Preparation of ACEL Thin Films, Third Interim Report, June 1989
4) The Preparation of ACEL Thin Films, Fourth Interim Report, September 1989
5) The Preparation of ACEL Thin Films, Fifth Interim Report, November 1989
6) The Preparation of ACEL Thin Films, Sixth Interim Report, January 1990
7) A Saunders and A Vecht, Novel Techniques for TF EL, Electroluminescence, Springer Proceedings in Physics, Vol. 38, Edit. S Shionoya and H Kobayashi, Proceedings of 4th International Workshop, Tottori, Japan, Oct 11-14 1988 p. 228-231.

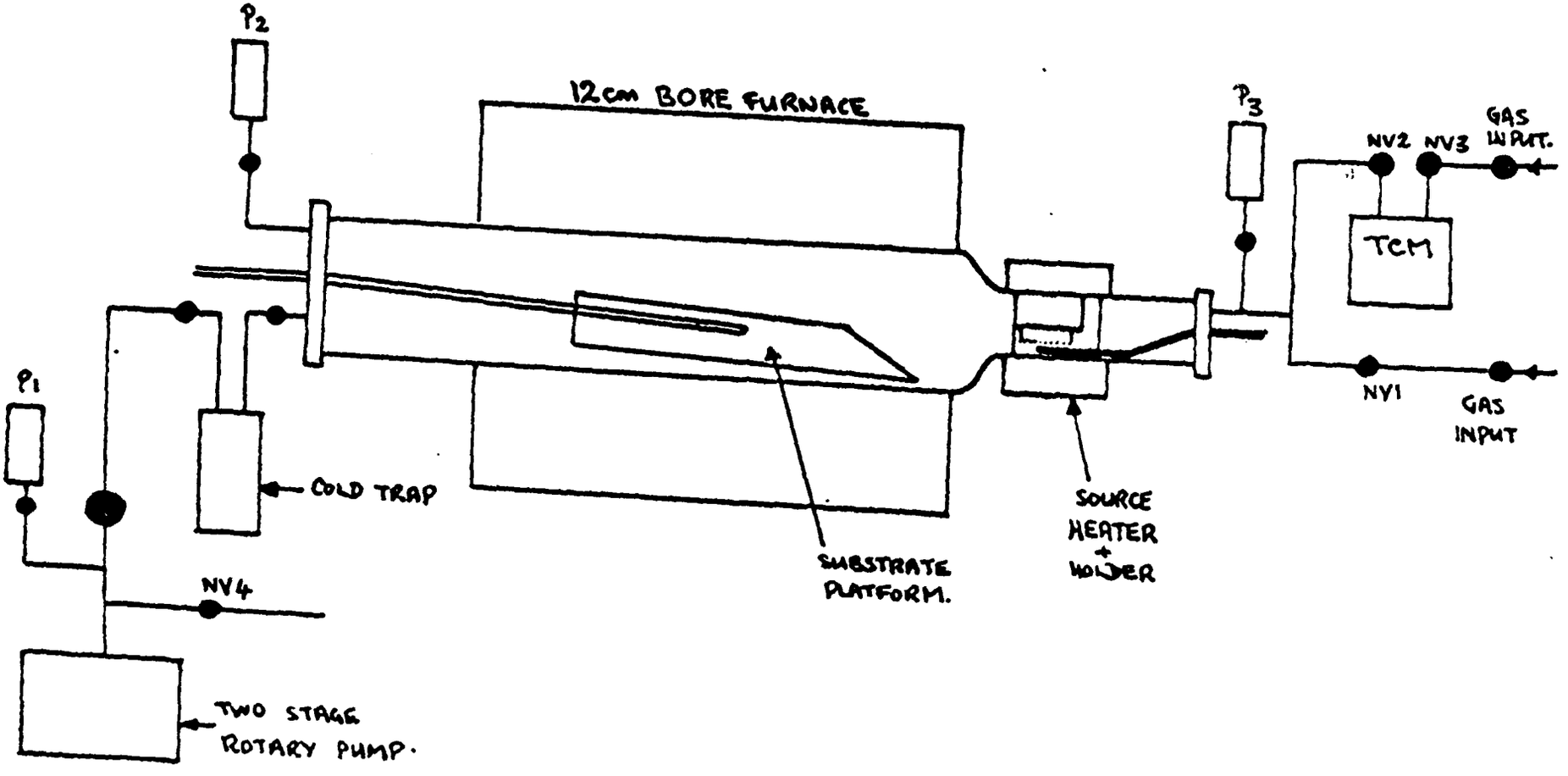

P2
12cm BORE FURNACE
P3
NV2
NV3
GAS INPUT.
TCM
P1
COLD TRAP
NV1
GAS INPUT
SOURCE HEATER + HOLDER
SUBSTRATE PLATFORM.
NV4
TWO STAGE ROTARY PUMP.

Fig 1.

Fig. 2

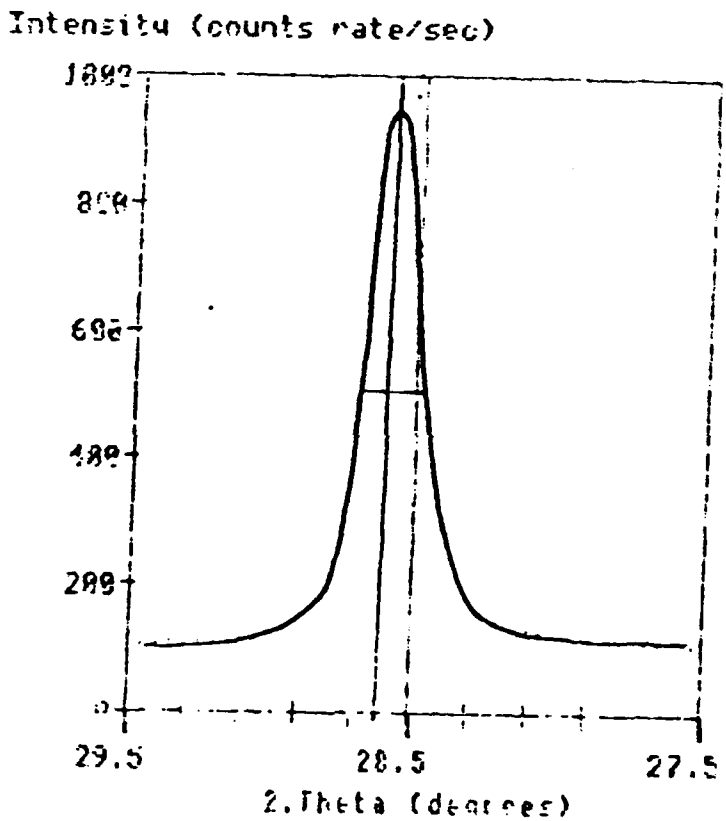


Fig. 3. **L-V Characteristics of Various Mn Sources**

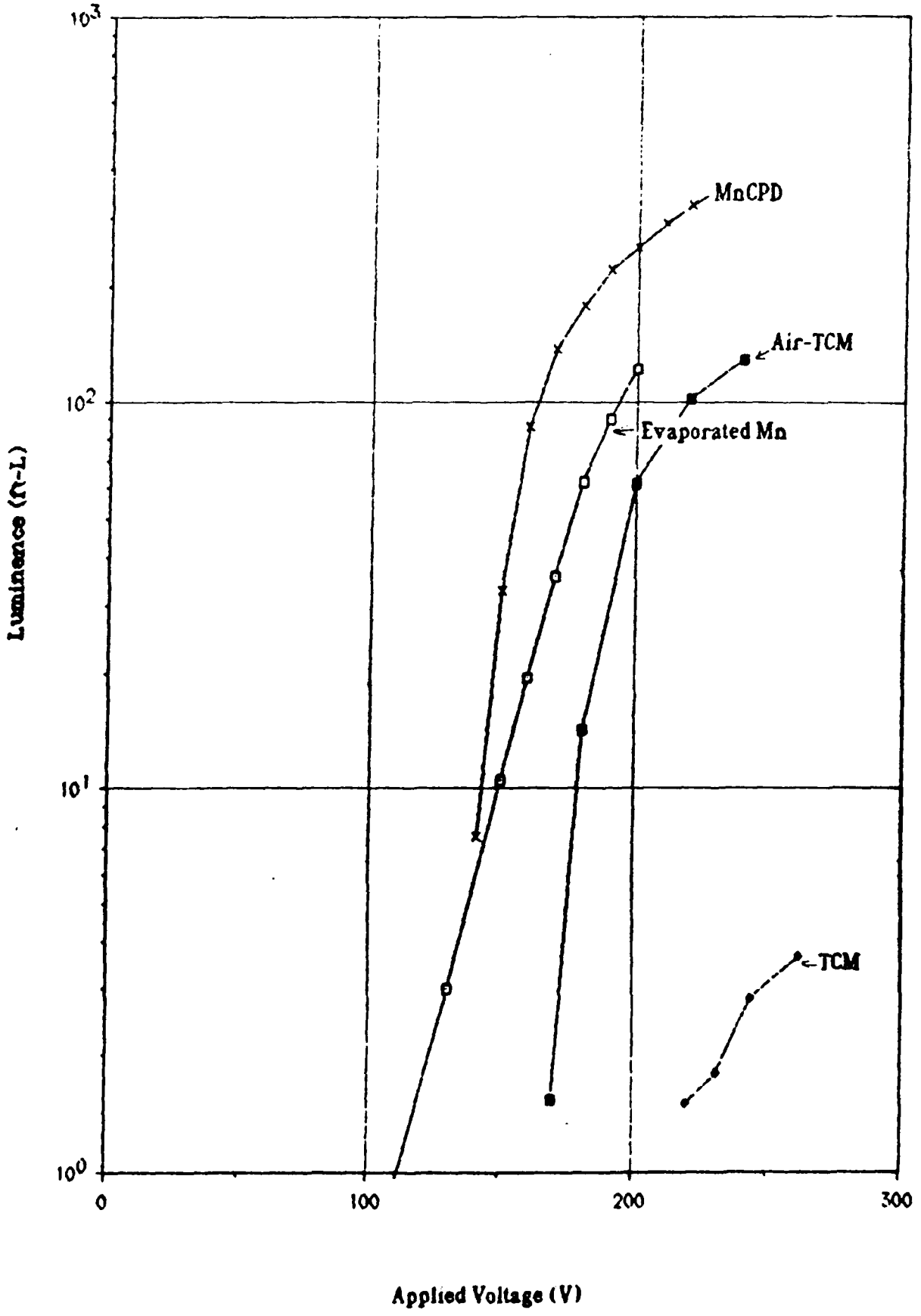


Fig. 4 Spray Pyrolysis System

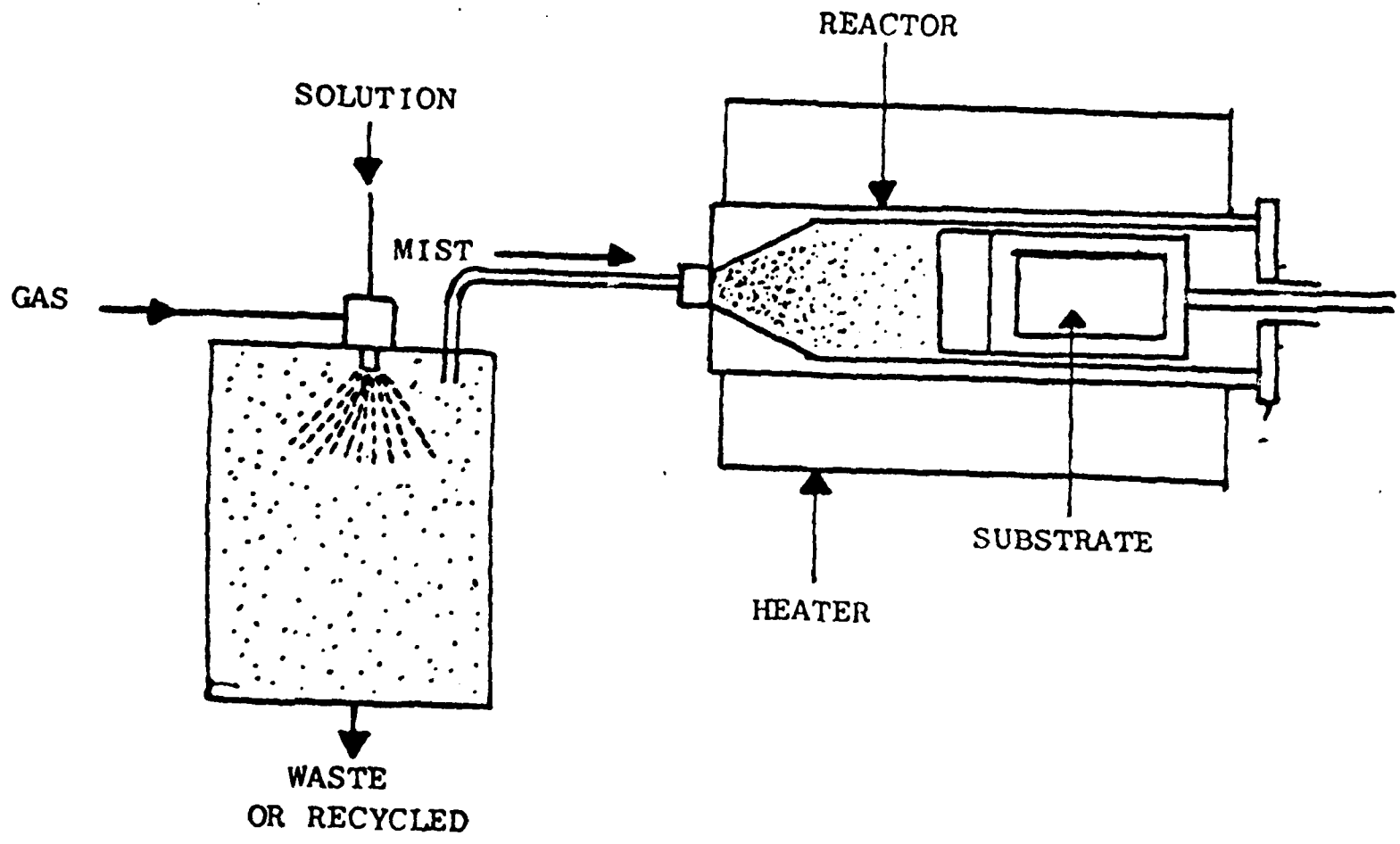


Fig. 5.

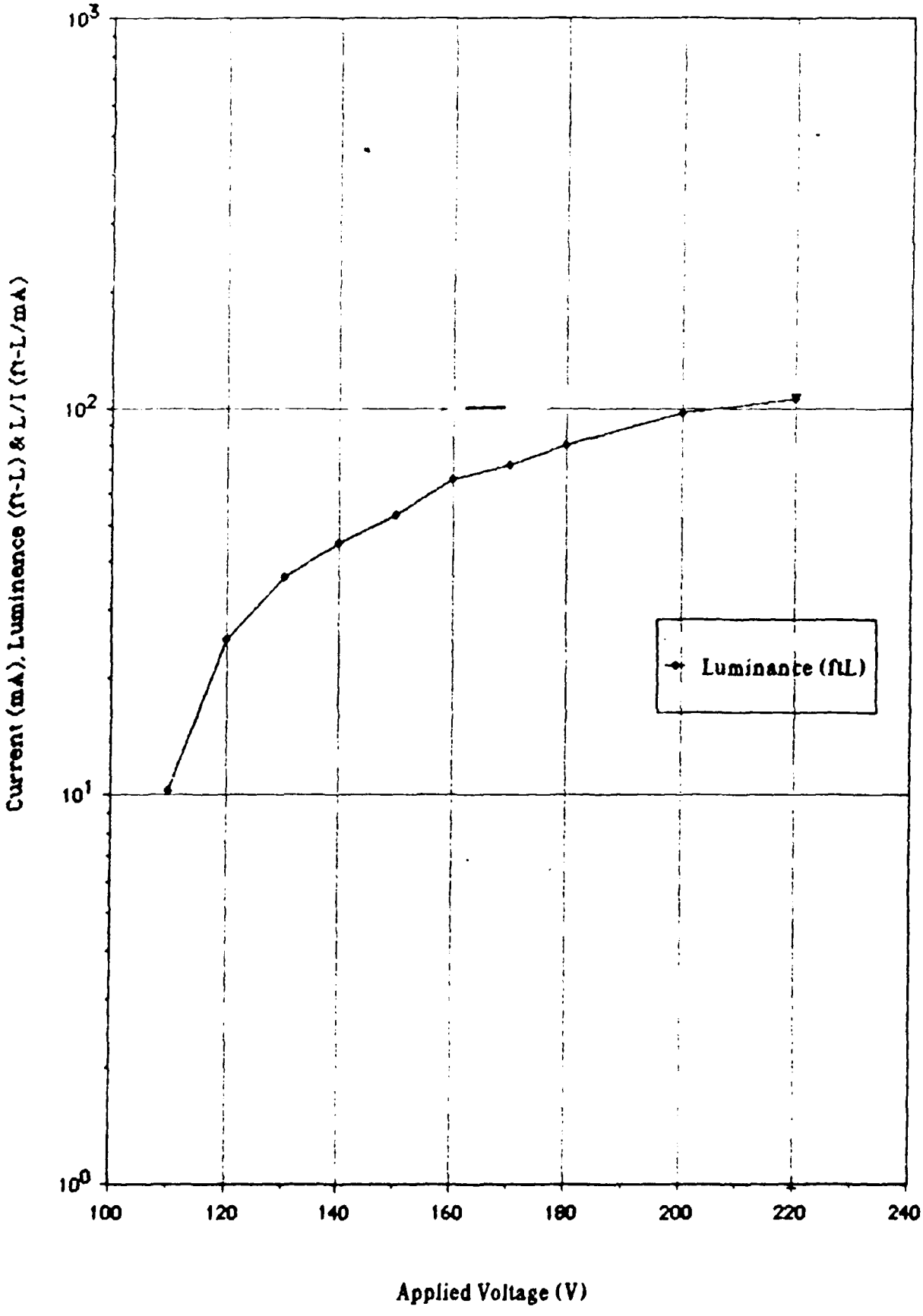
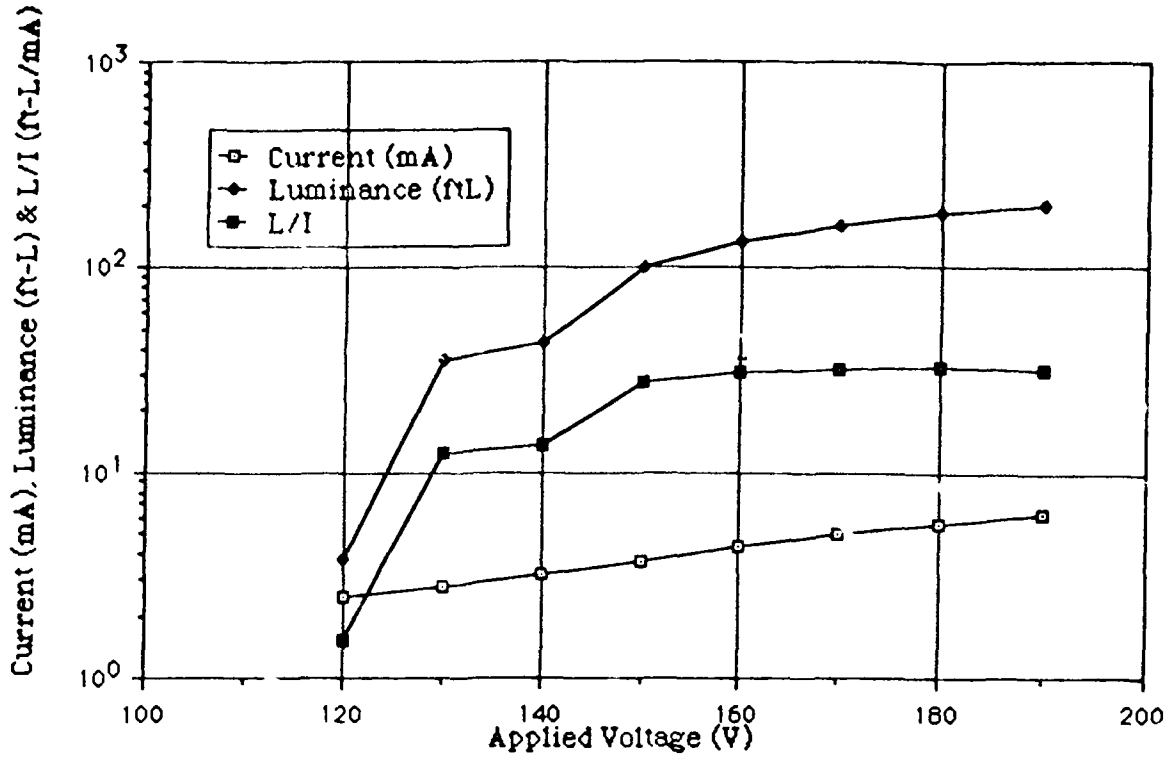
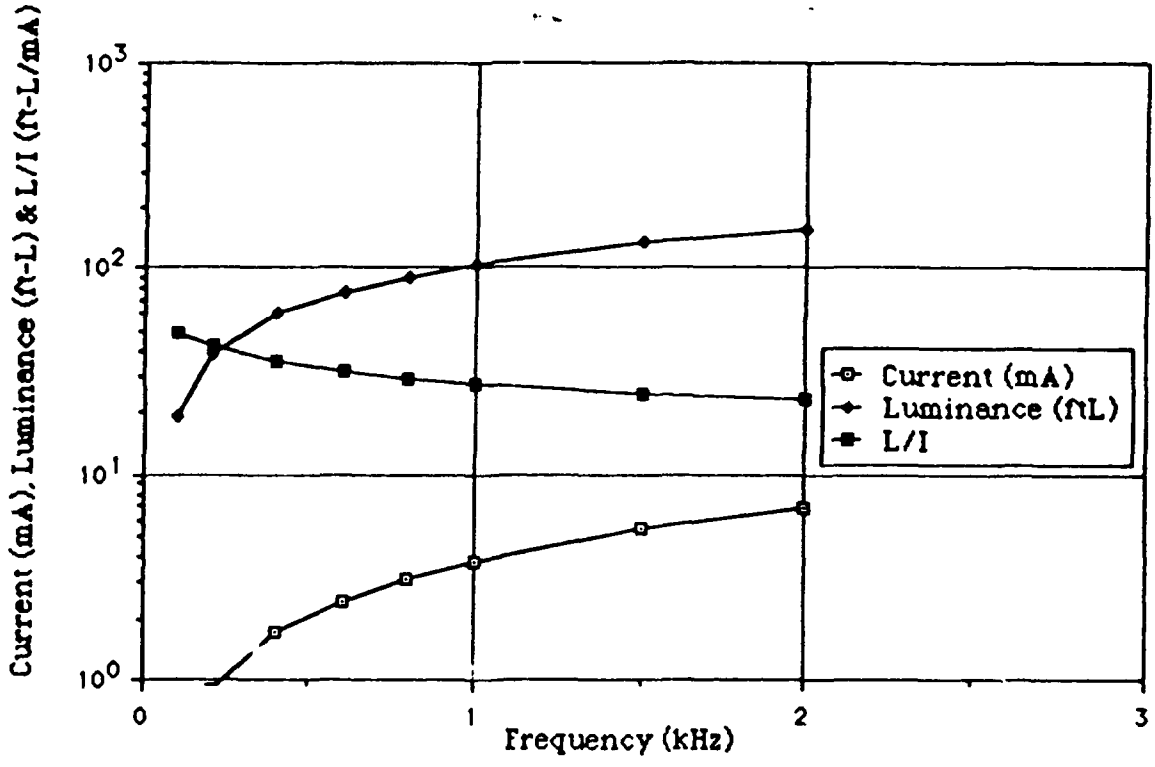

10^3
10^2
10^1
10^0
100
120
140
160
180
200
220
240
Current (mA), Luminence (ft-L) & L/I (ft-L/mA)
Applied Voltage (V)
Luminance (ftL)

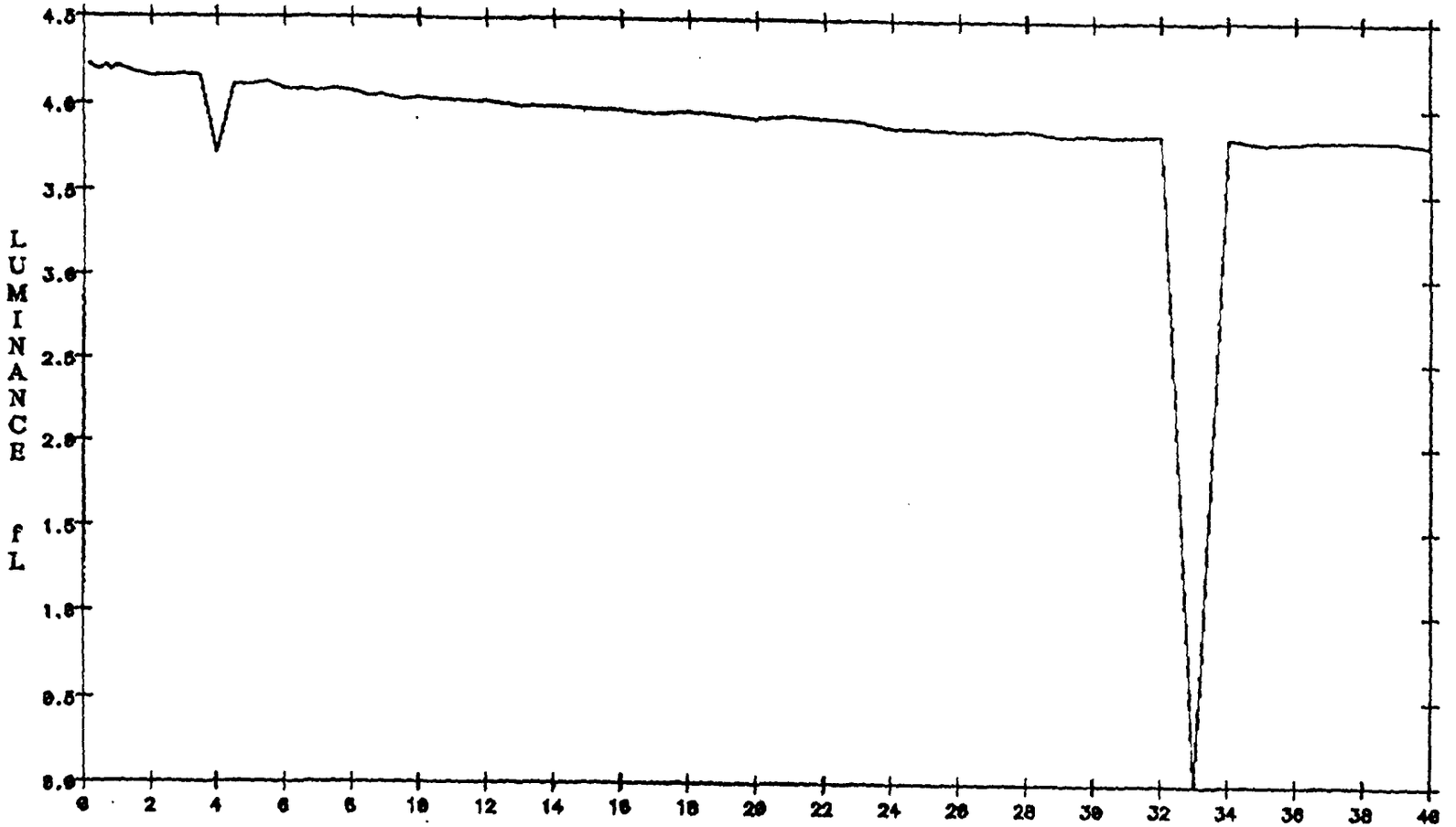
Fig. 6.


Current (mA), Luminance (ft-L) & L/I (ft-L/mA)
10^3
10^2
10^1
10^0
Current (mA)
Luminance (ftL)
L/I
100
120
140
160
180
200
Applied Voltage (V)


Current (mA), Luminance (ft-L) & L/I (ft-L/mA)
10^3
10^2
10^1
10^0
Current (mA)
Luminance (ftL)
L/I
0
1
2
3
Frequency (kHz)

Manufacturer AVECHT Sample#102 LABCOM# AE102Y Date Received 03/10/90 Tested 03/28/90 Color YEL
Lit Area 0.00000 cm*2 Cap/cm*2 0.0 (pF) V1max 250 Pulse 1 30 us Delay 0.5 ms
Data File 900328080011.DAT # of Pixels Lit 6 V2max 250 Pulse 2 30 us Frequency 100 Hz
VECHT MN SAMPLE:AVA301

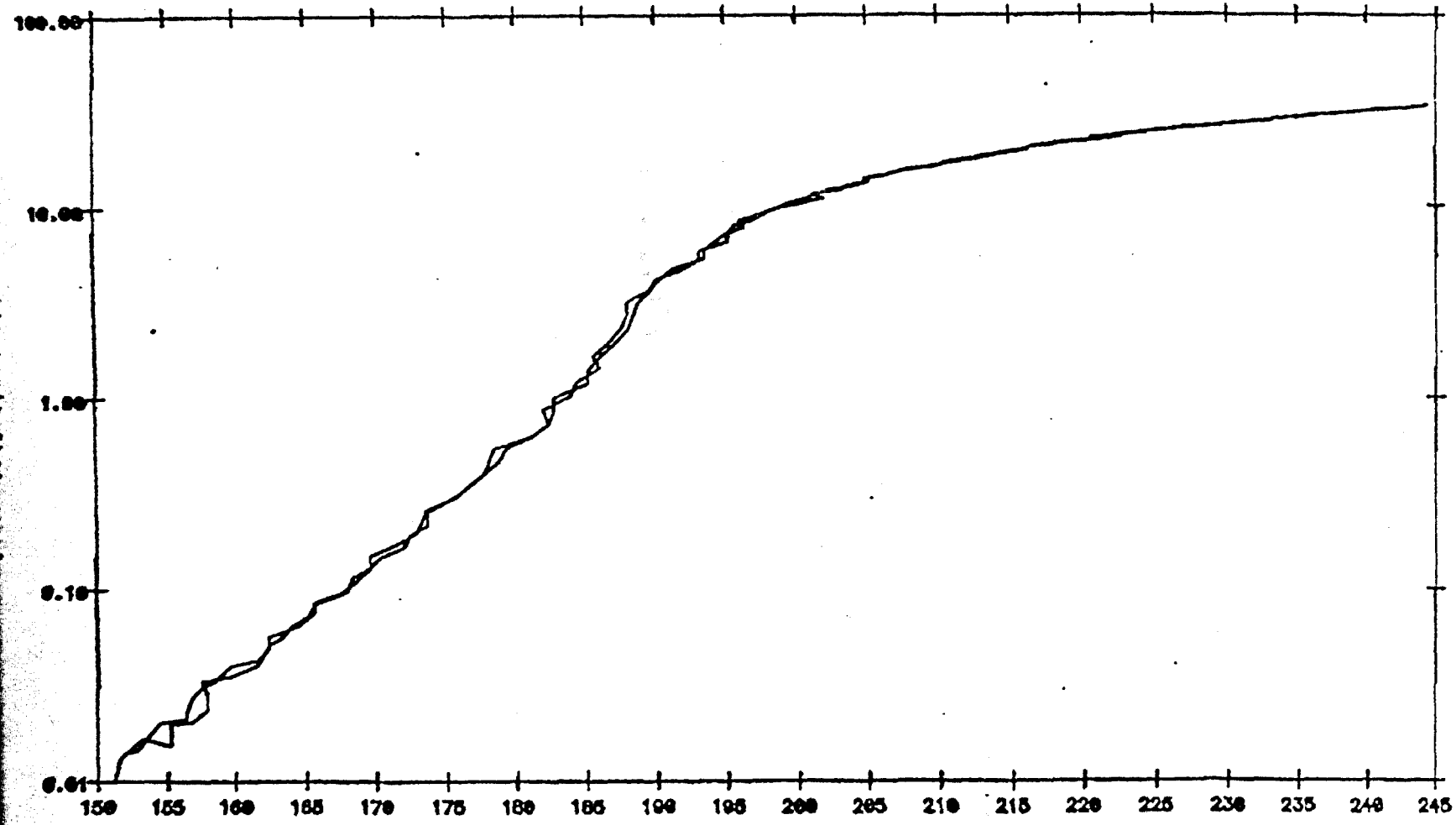
Fig. 7. STABILITY OF LIGHT OUTPUT OVER TIME



US Army Electronic Devices & Technology Laboratory
STS data file 900328080011

anufacturer AVECHT Sample#105 LABCOM# AE105Y Date Received 03/10/90 Tested 03/28/90 Color YEL
t Area 0.24300 cm*2 Cap/cm*2 0.0 (pF) V1max 250 Pulse 1 30 us Delay 6.0 ms
ata File 900328134016.DAT # of Pixels Lit 8 V2max 250 Pulse 2 30 us Frequency 100 Hz
ECHT MN SAMPLEAVA304 LUM WITH DAMPING

Fig. 8. LUMINANCE VS APPLIED VOLTAGE



S Army Electronic Devices & Technology Laboratory
TS data file 900328134016